Understanding the Potential Toxic Properties of Lunar Dust

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Outline

- Motivation
- Materials
- Activation and Monitoring of Lunar Dust and Analogs
  - Fluorescence
  - EPR
- Solubility Studies
  - ICP-MS
- Cellular Toxicity
  - A549


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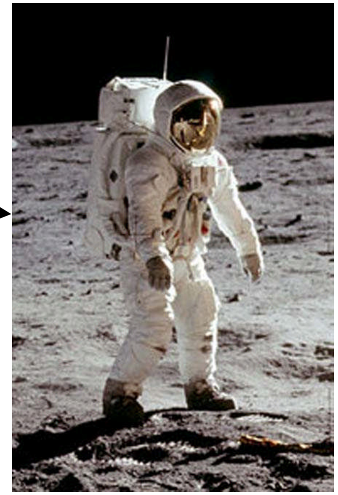
Words of Wisdom

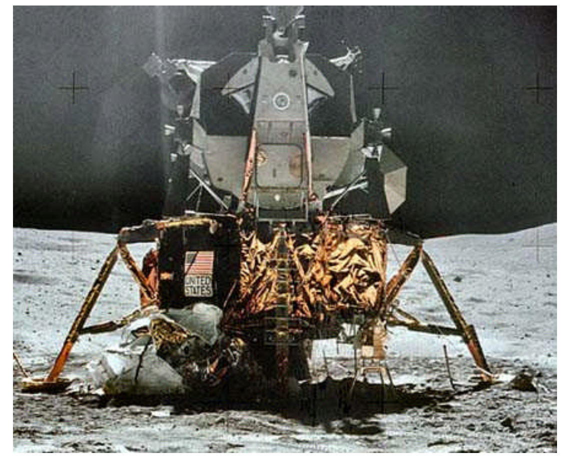
"I think dust is probably one of our greatest inhibitors to a nominal operation on the Moon. I think we can overcome other physiological or physical or mechanical problems except dust."

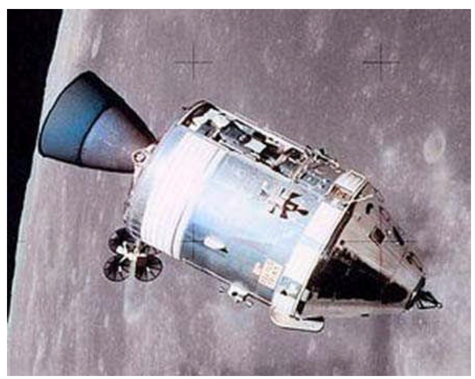
Gene Cernan
Apollo 17 Technical Debrief


Dust clings to Eugene Cernan's suit after a 1972 moonwalk.

Pathway of Dust Introduction







Lunar EVA Suits

Jack Schmitt
(Apollo 17)

Problems Caused by Dust

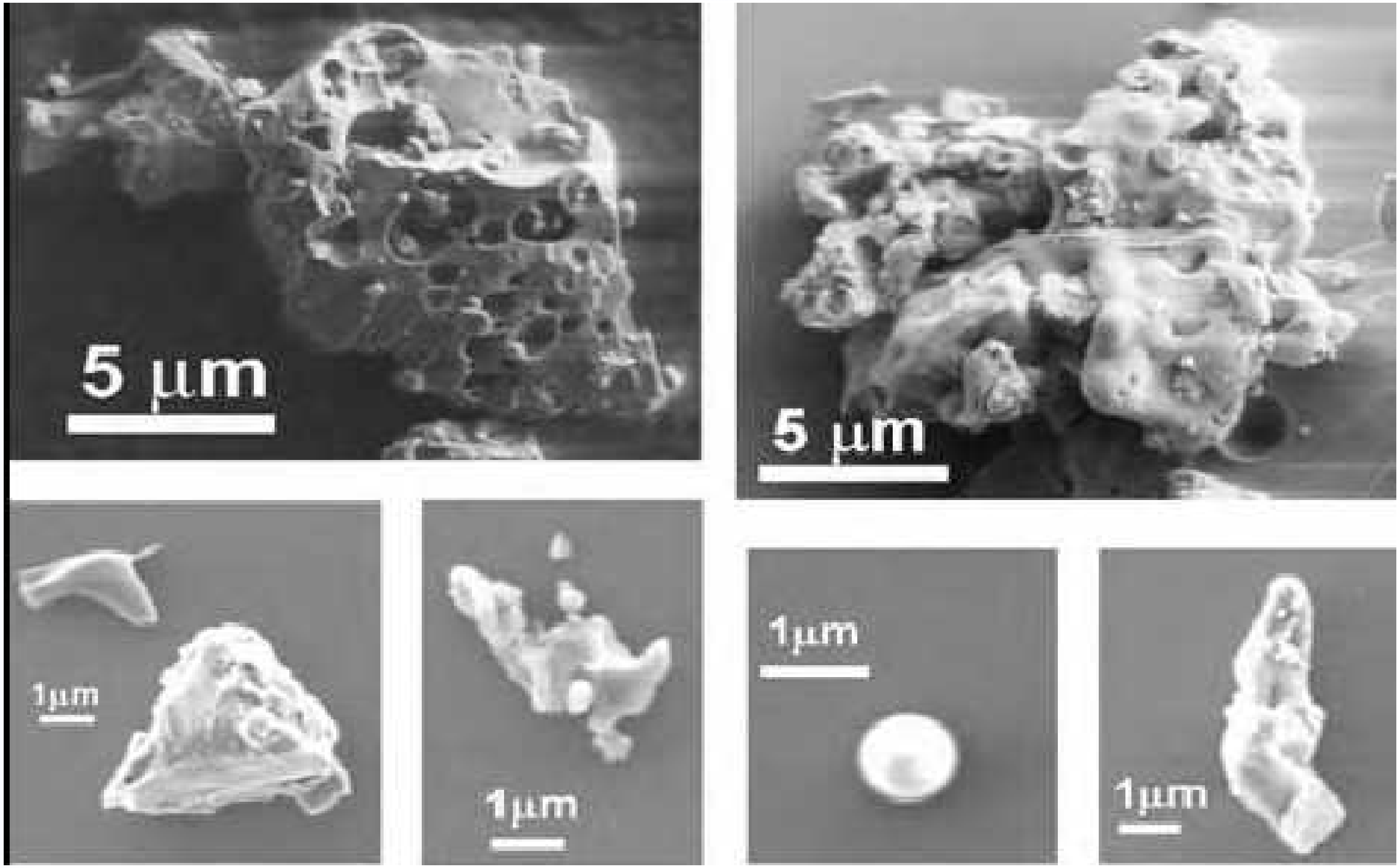
- Obscured vision
  - Apollo 15: vision completely obscured below 60 ft when landing
- Clogged equipment
  - Apollo 12: wrist and suit hose locks clogged with dust
- Coated surfaces
  - Apollo 11: T.V. cable caused tripping after dust covering
- Inhalation
  - Apollo 15: gunpowder smell
  - Apollo 17: “hay fever” symptoms
- Degraded radiators
  - Apollo 16: degraded instrument performance from overheating
- Fooled instruments
- Caused seal failure
  - Apollo 14: measurable leaking of suits
- Abraded surfaces
  - Apollo 16: gauge dials unreadable from scratching

What *is* lunar dust?

- Lunar soil is defined as the loose fragmental material with a grain size smaller than 1 cm on and near the surface of the moon. It is a subset of the lunar regolith which includes all size fragments including boulders.

- Lunar dust is the finest size fraction of lunar soil. A working definition of lunar dust is that it is all grains smaller than 20 µm.

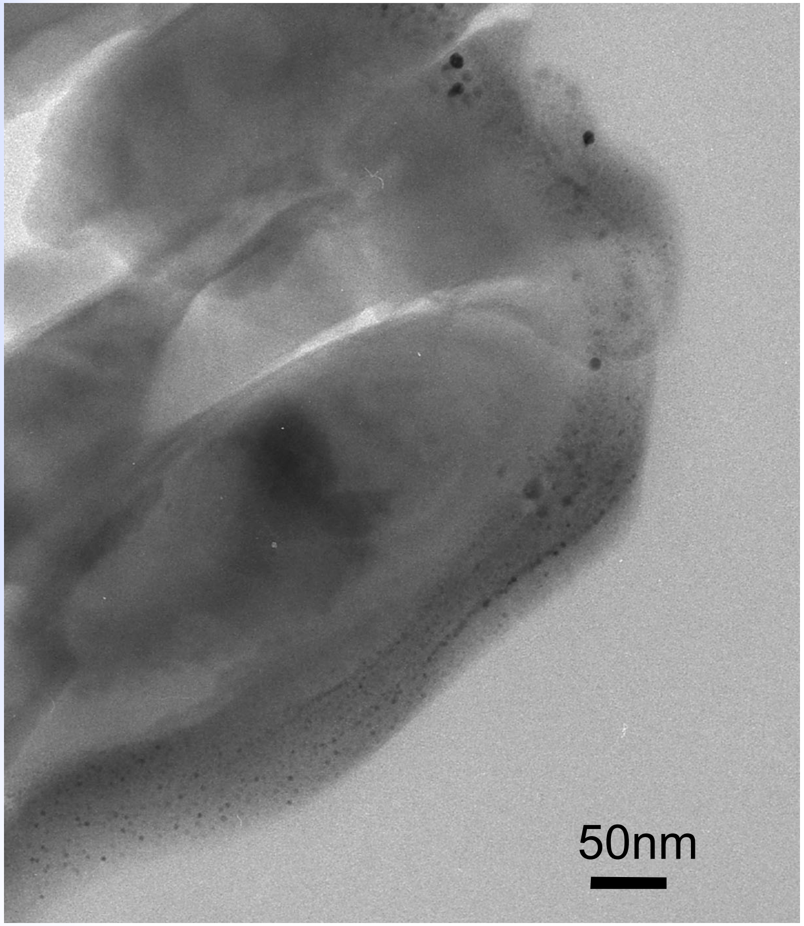
Lunar Dust

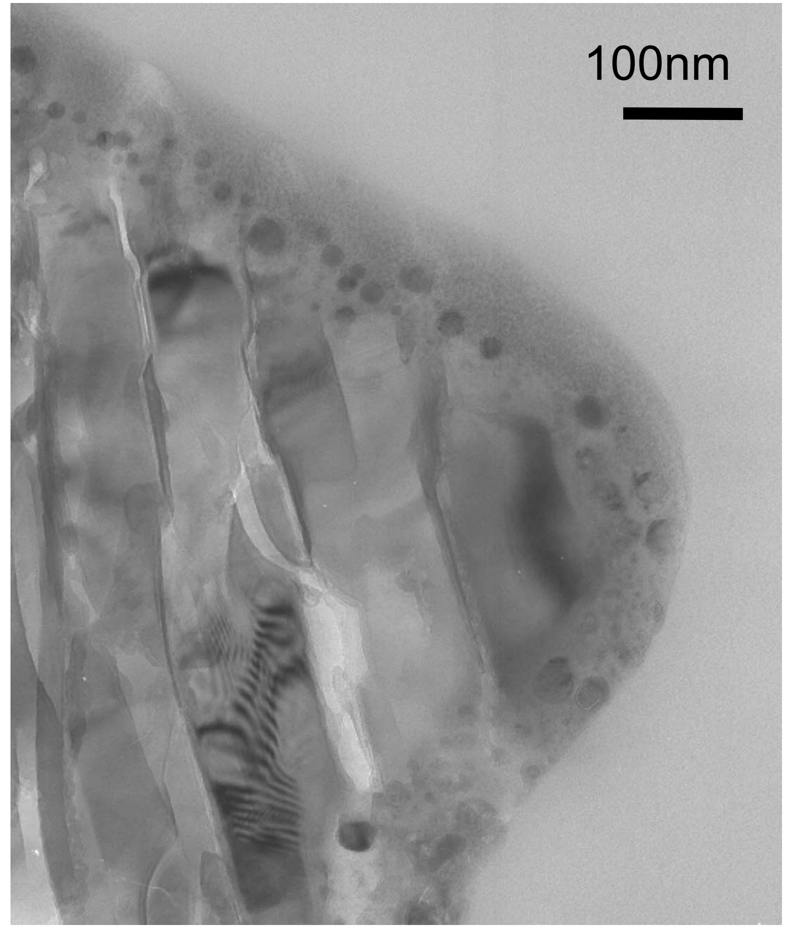


- Contains Si-containing minerals, various oxides, and trace metals
- Magnetic
- Particles are oddly shaped, with jagged edges, and do not pack together well

Sarah Noble, MSFC

Lunar Dust Rims

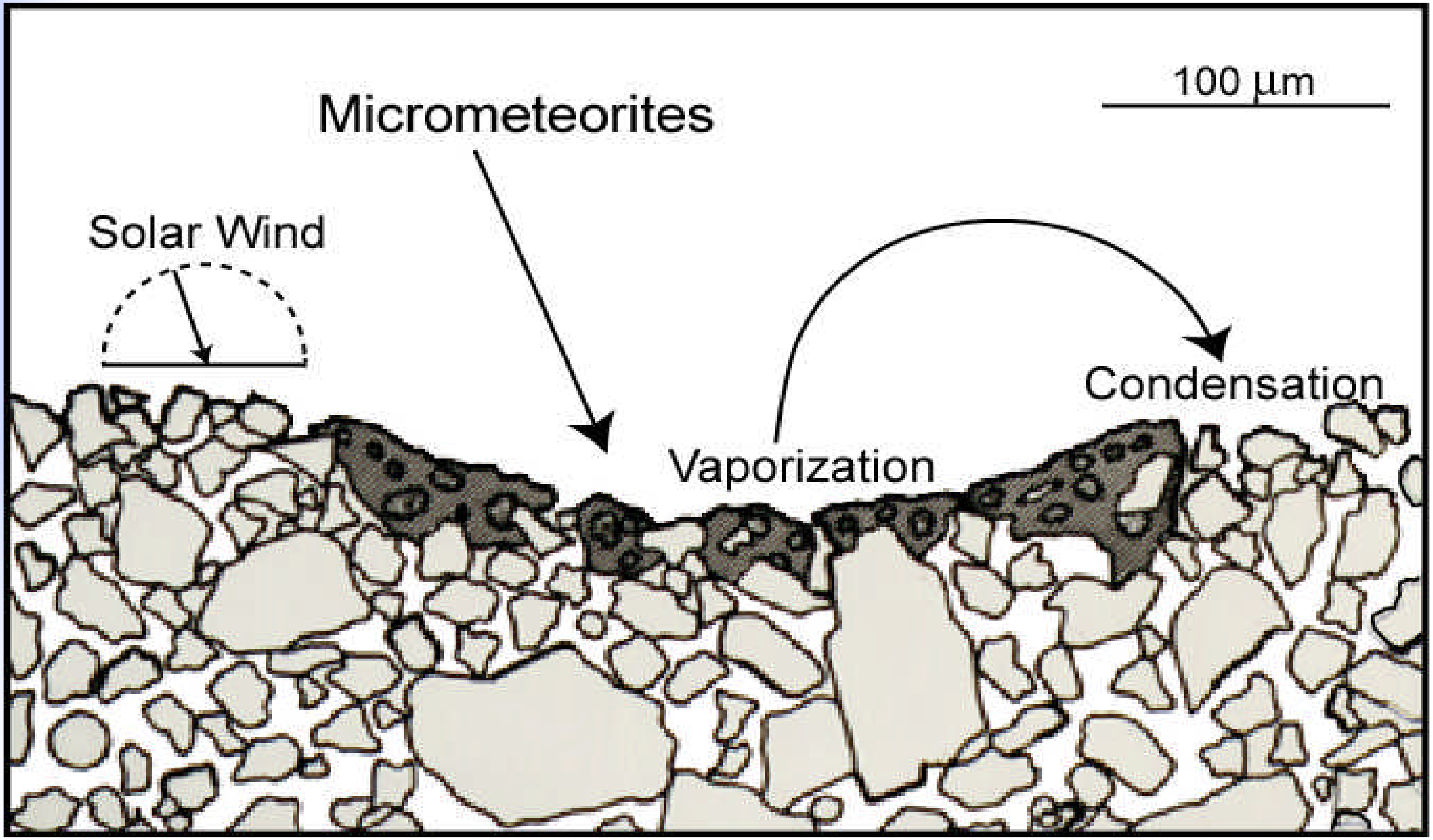




Glassy rims produced by vapor/sputter deposition. Also contain ~ 10 nm Fe nanoparticles

Sarah Noble, MSFC

Lunar Soil Formation



Lunar soil is formed by a combination of comminution (breaking down), agglutination (clumping together), and vapor deposition.

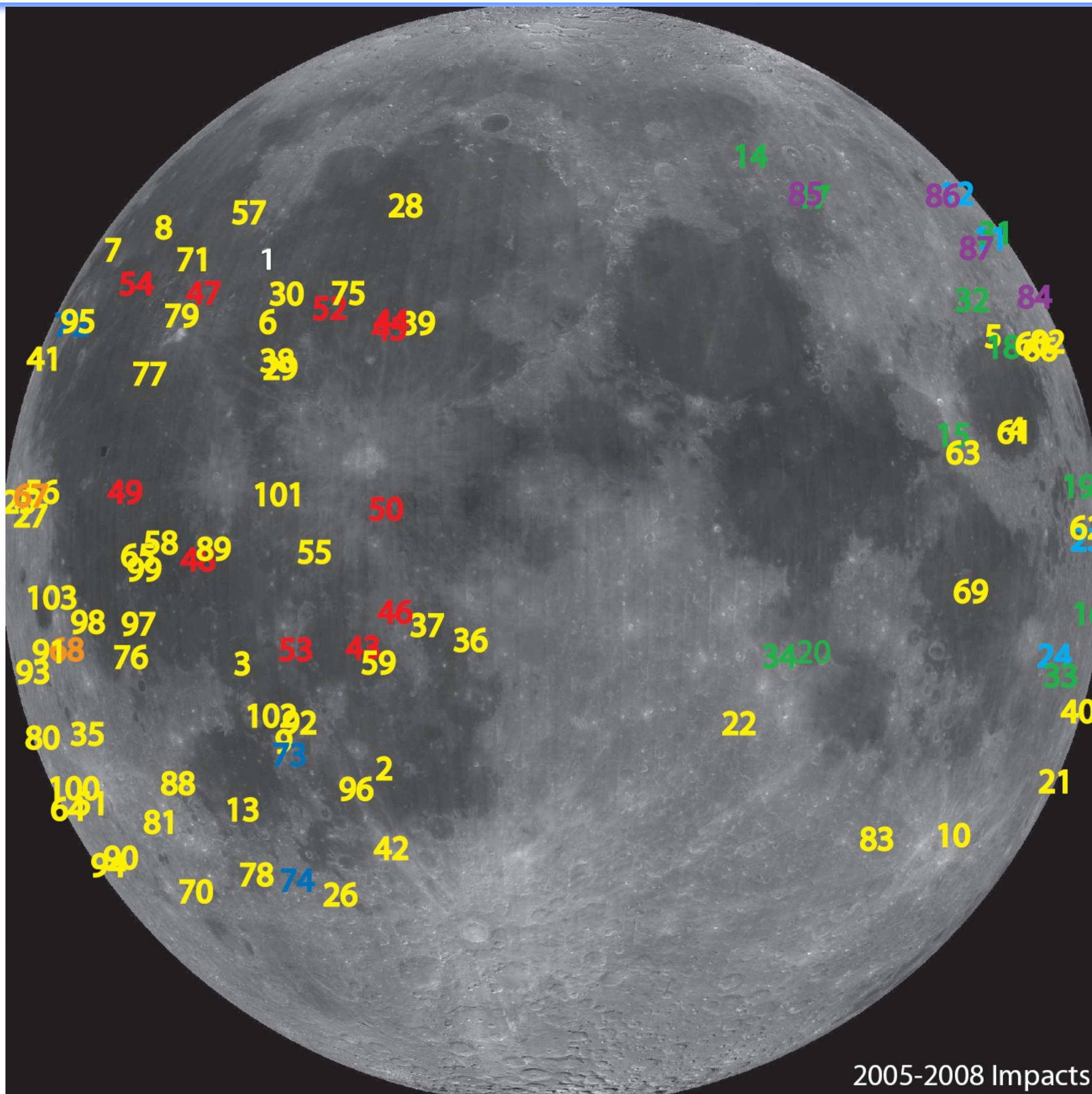
Larry Taylor, U. Tennessee

Meteorite Impact on the Moon

- 25 cm diameter meteorite traveling at 85,000 mph
- Kinetic energy of impact: 17 billion joules (equivalent to 4 tons of TNT)
- New crater: 14 meters wide by 3 meters deep
- Flash only 0.4 seconds in real-time

http://science.nasa.gov/headlines/y2006/13jun_lunarsporadic.htm

Recent Impacts



Lunar Dust Simulant (JSC-1A-vf)

Only 842 lbs of material returned from the moon!
Simulant material needed for preliminary studies.

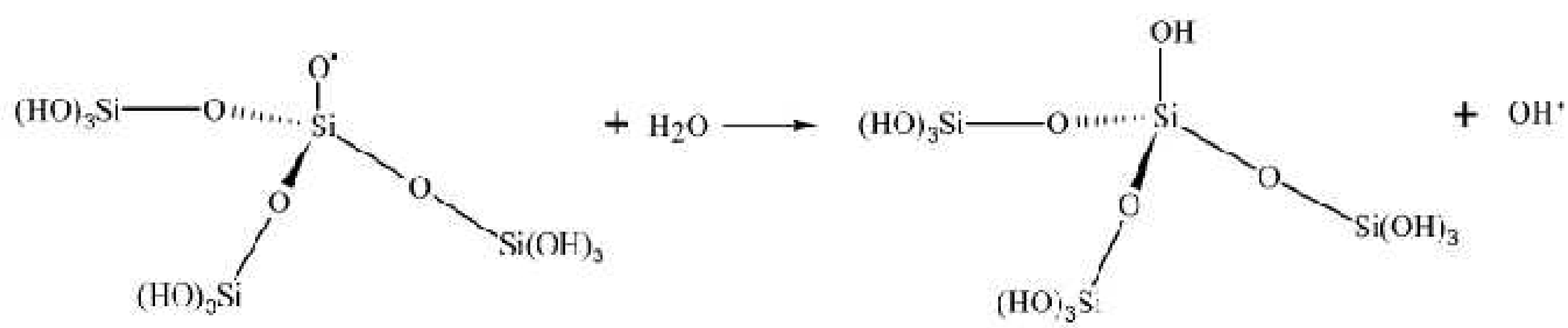
- Made from volcanic ash
- 50% SiO_2
- 42-45% other oxides (Al_2O_3, FeO, MgO, CaO)
  - Materials not pure oxides (mineral form)
- No trace metals
- Size distribution of particles similar to samples of lunar dust
- 90% smaller than 13 μm diameter
  - 50% < 3 μm

Lunar Dust Activation

- Constant activation of lunar dust by meteorites, UV radiation, and elements of solar wind
- No passivating atmosphere
- Active dust could produce reactive species in the lungs
  - Freshly fractured quartz
- Must determine methods of deactivation before new lunar missions
- First, must understand how to *reactivate* dust on Earth

What Does "Activated" Mean?

- Presence of reactive sites on surface
  - Free radicals
- Ability to produce reactive species in solution

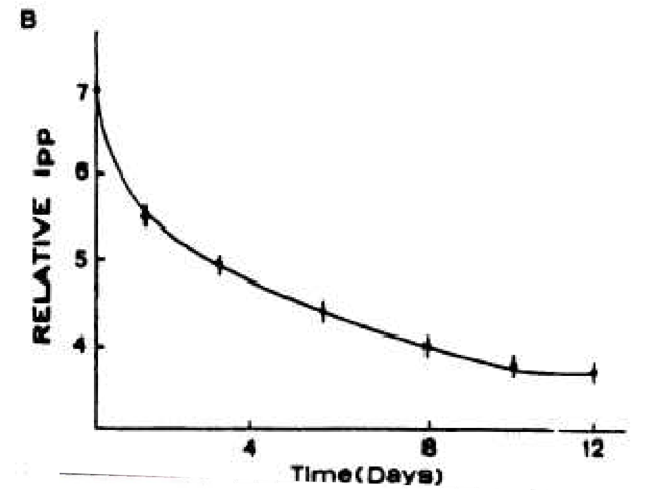


Reaction 5

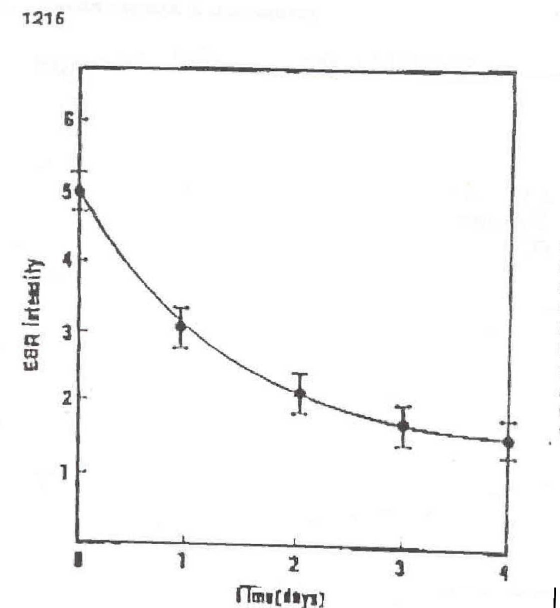
J. Narayanasamy and J.D. Kubicki, *J. Phys. Chem. B* **109** (2005) 21796-21807

Previous Studies of Quartz Activation

- Grinding quartz gives electron spin resonance (ESR) signal characteristic of Si· or Si-O· radicals
- Increased grinding time produces higher signal
- Decrease in Si-based radicals over time in air
    - Half-life of ~30 hours, with 20% of signal detectable even after 4 weeks



- Ground quartz in aqueous solution produces OH radicals
- Radical production decreases with exposure to air
    - Half life of ~ 20 hours



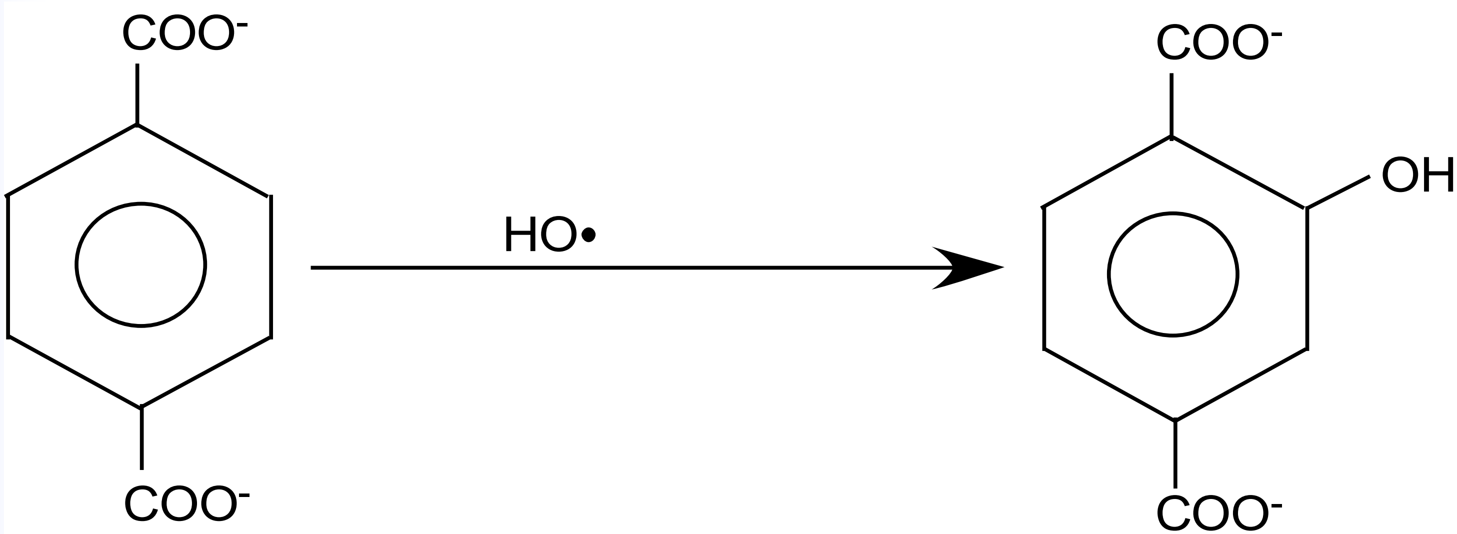
V. Castranova, *Environ. Health Perspect*. **102** (1994) 65-68.
V. Vallyathan *et al*., *Am. Rev. Respir. Dis*. **138** (1998) 1213-1219

Activation Methods Tested

- Crushing/Grinding
  - Mortar and pestle
  - Ball Mill
- UV activation
- Heating

Fluorescence

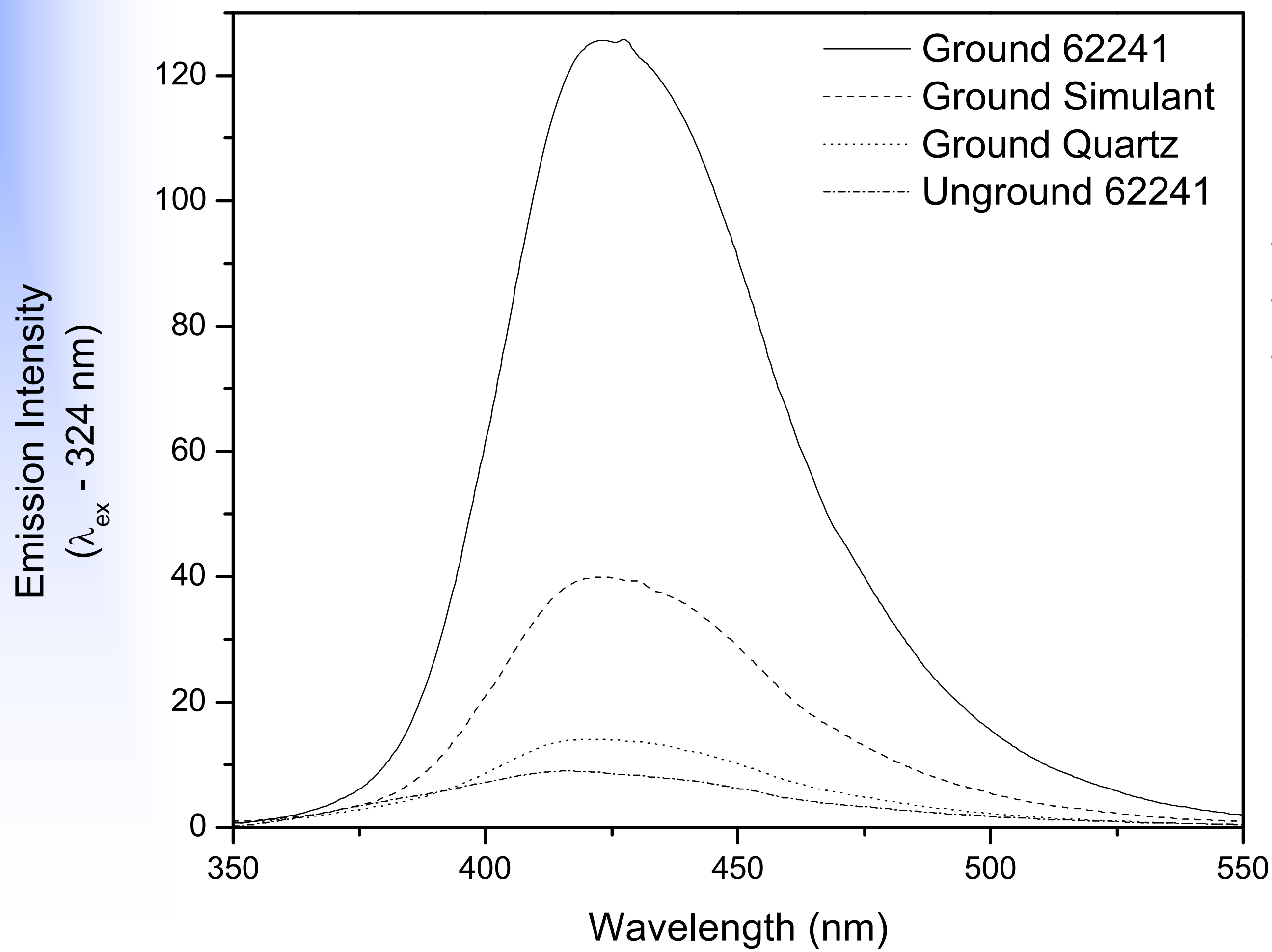
Hydroxyterephthalate as a Probe of Hydroxyl Radical Generation



Terephthalate (non-flurorescent)

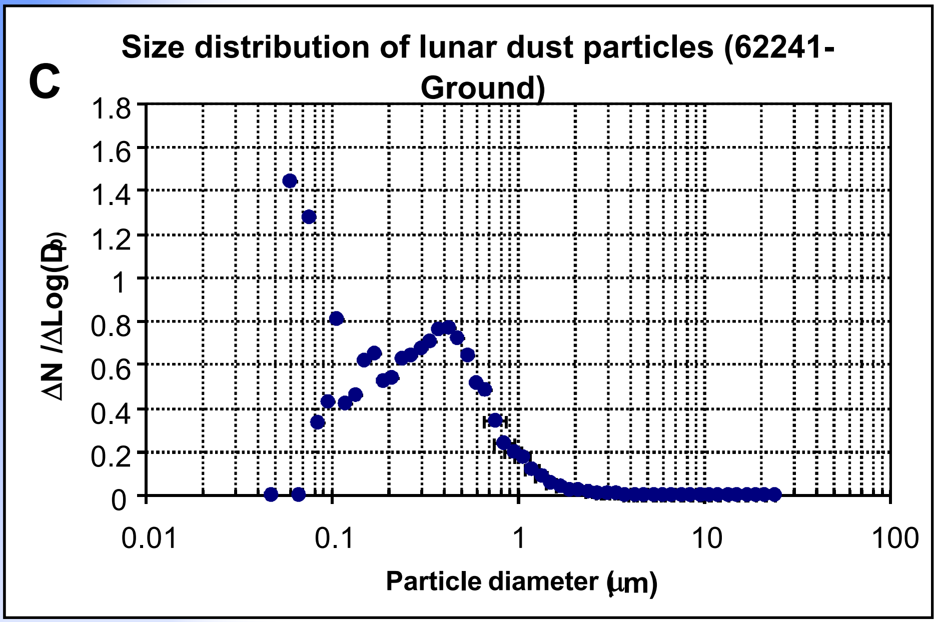
2-Hydroxyterephthalate (fluorescent)

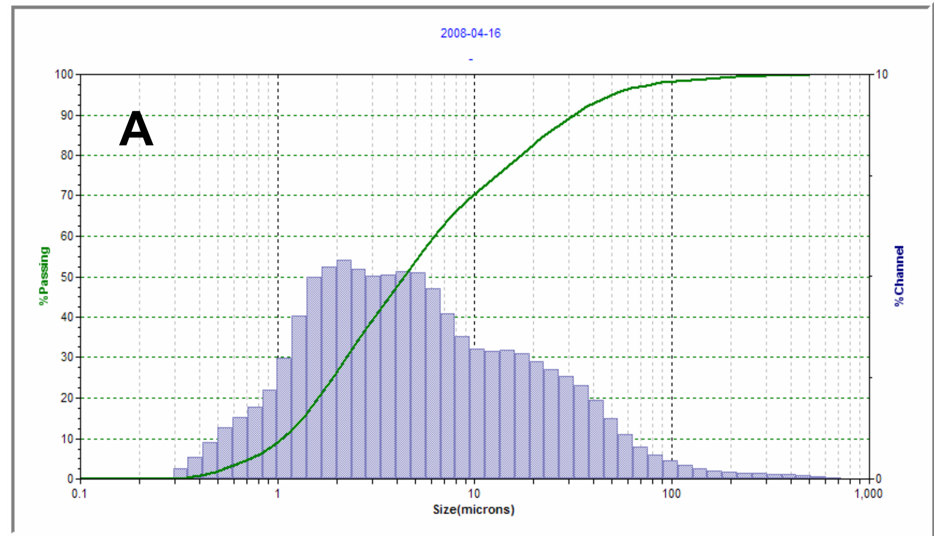
Activity Comparison of Ground Lunar Soil, Lunar Simulant, and Quartz

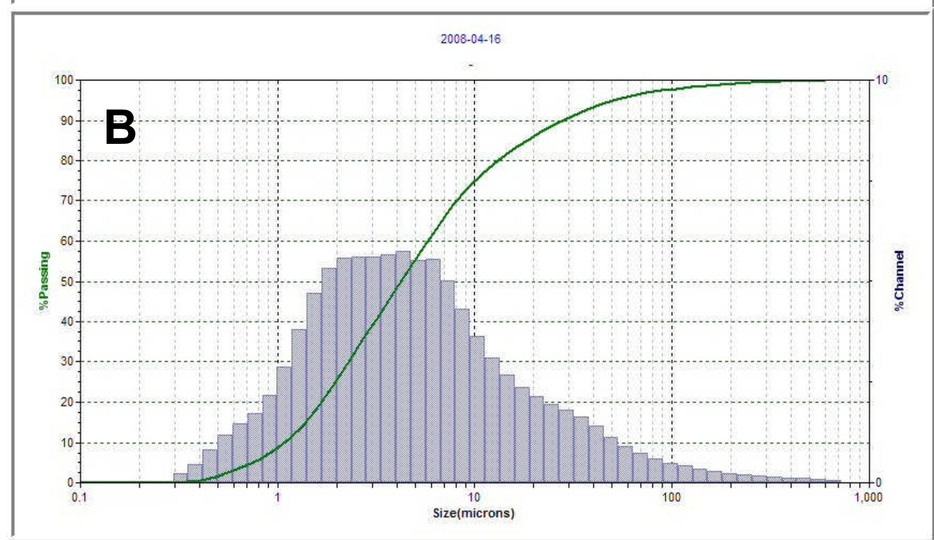


- 10 minute grinding
- 3.8 mg/mL JSC-1A-vf
- 10 mM Terephthalate

Size Distribution after Grinding



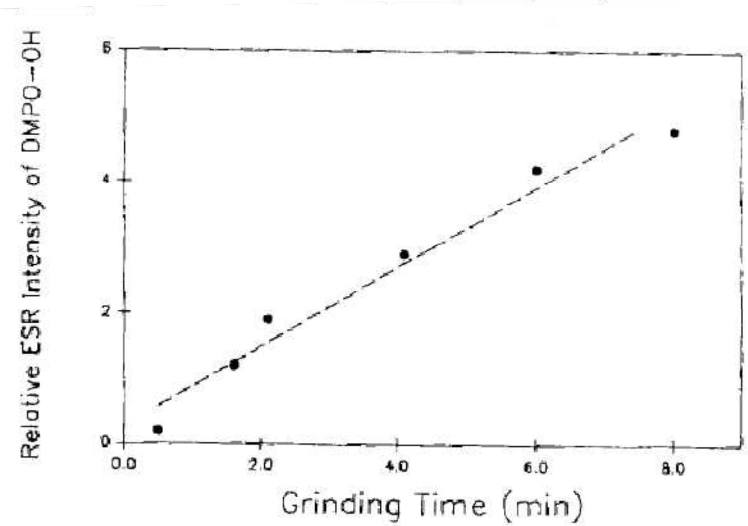


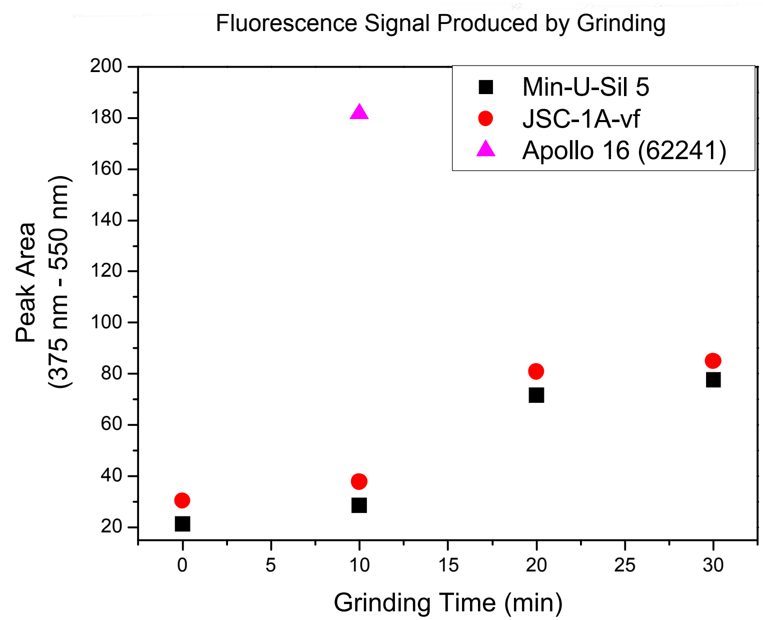


A: Min-U-Sil 15- 8.436 m^2/g
B: JSC-1A-vf- 5.369 m^2/g
C: 62241 (Apollo 16)- 8.404 m^2/g

Effect of Grinding Time

- Grinding time has a direct effect on amount of hydroxyl radicals produced upon addition of ground quartz to solution
- Grinding also shown to produce higher number of silicon-based radicals in ESR spectra
- Increase in hydroxyl production also seen for lunar simulant with increased grinding

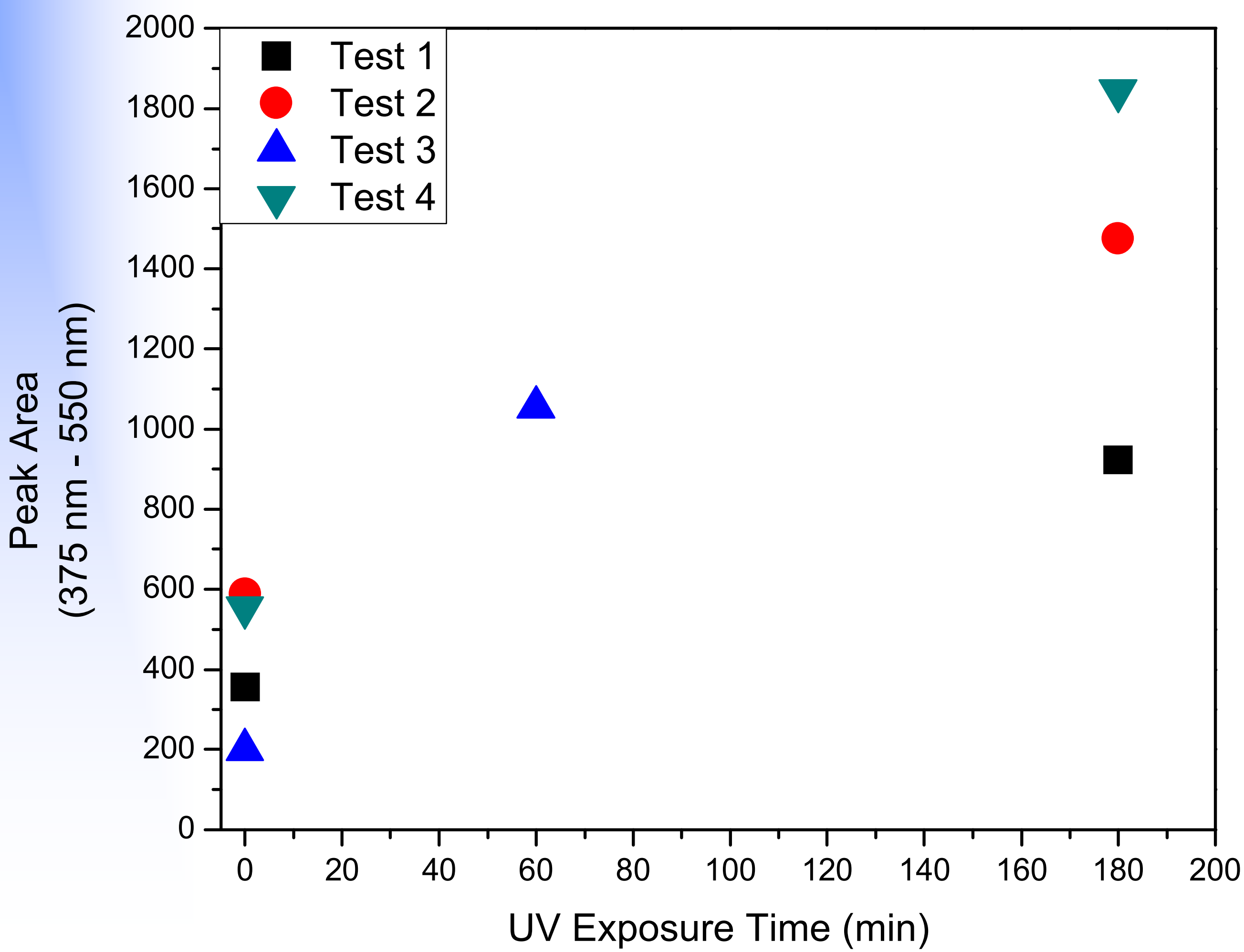




N.S. Dalal, X. Shi, and V. Vallyathan, *Free Rad. Res. Comms.* **9** (1990) 259-266.

Activation by UV Exposure and Heating

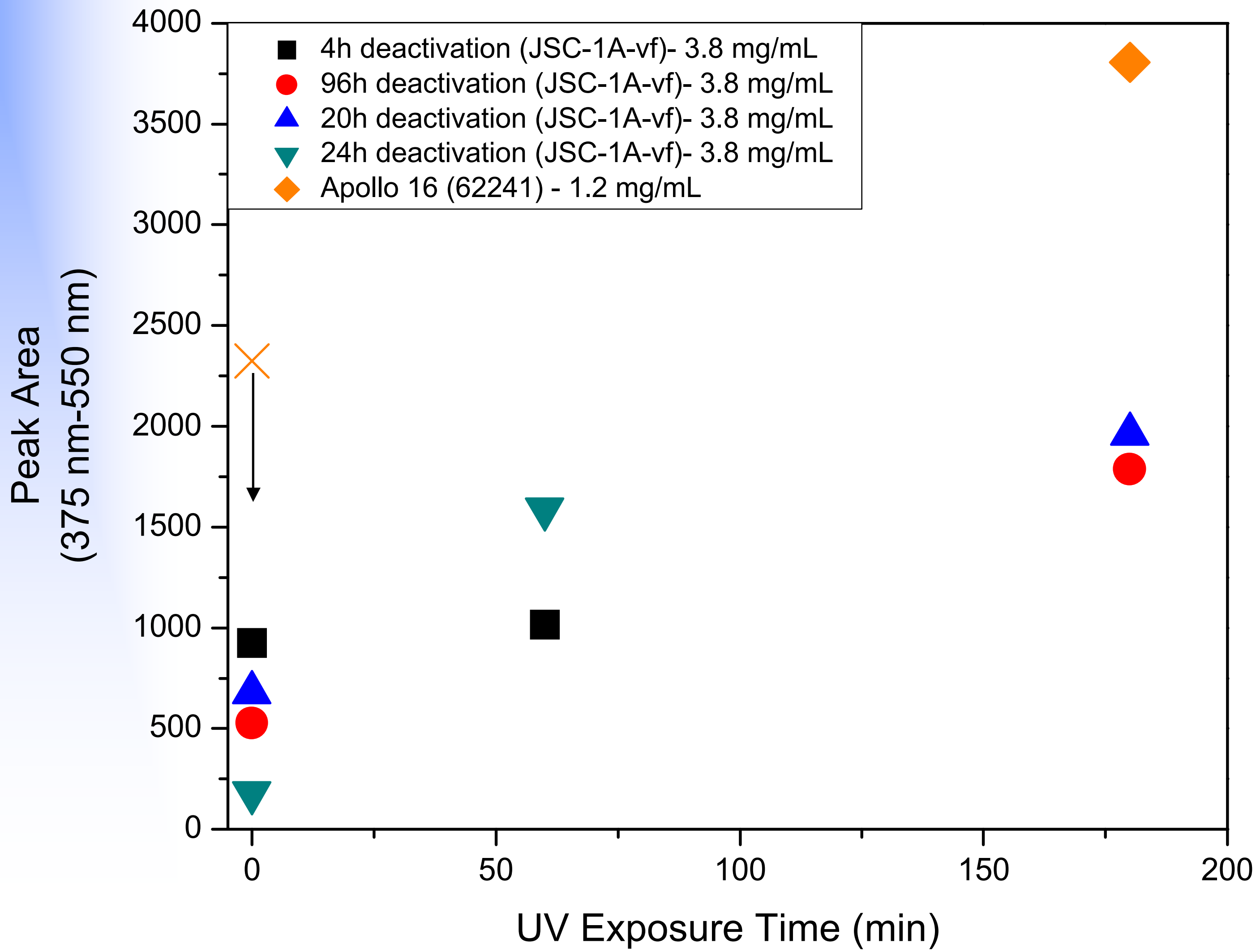
UV Activation of Unground Lunar Simulant



- 3.8 mg/mL JSC-1A-vf
- 10 mM Terephthalate
- 800 W UV (initial setting)
- ~ 5 X 10^{-4} Torr

Exposure of unground simulant to UV radiation under vacuum leads to the production of hydroxyl radicals by the simulant when placed in solution.

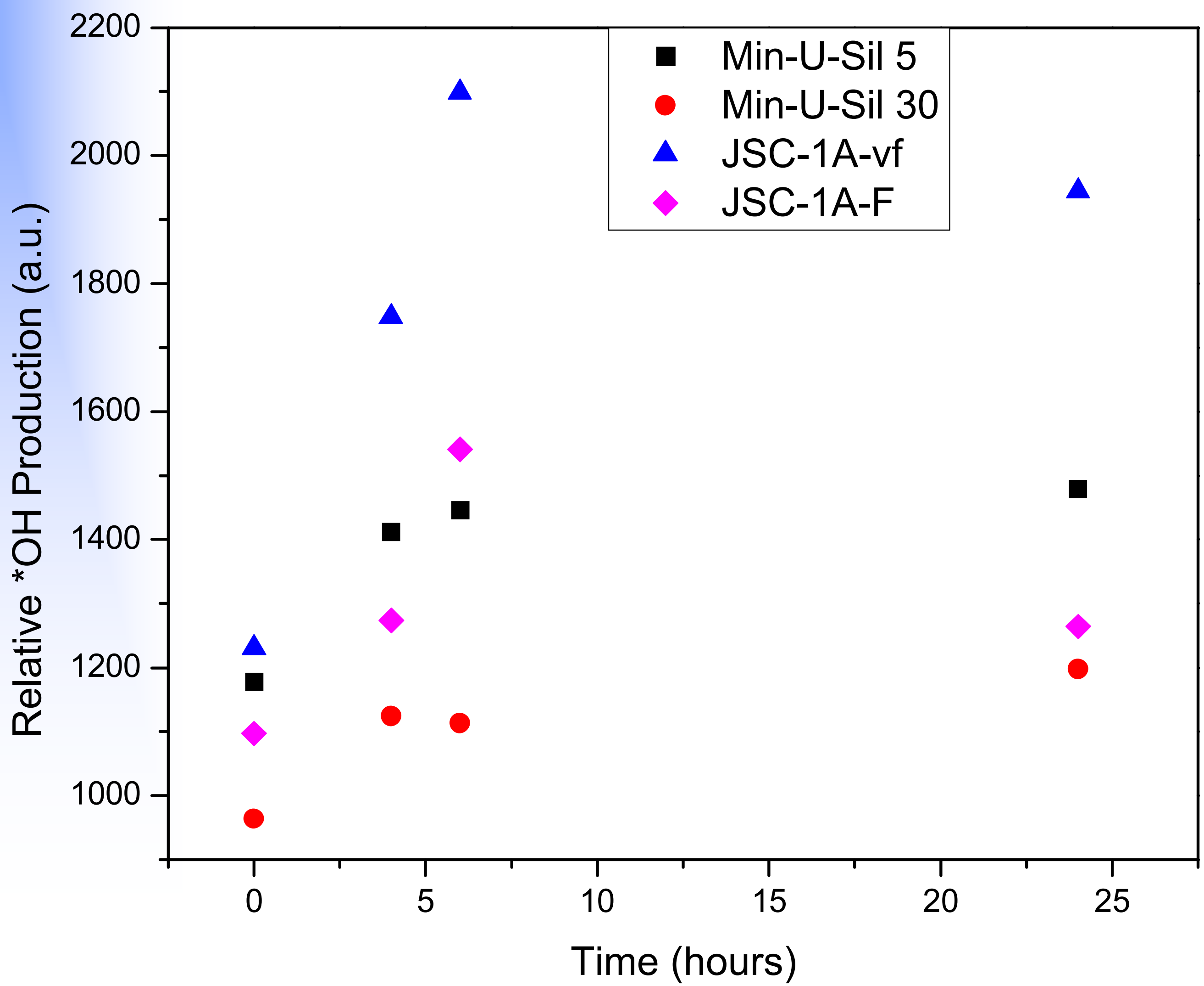
UV Reactivation of Ground, Deactivated Lunar Dust and Simulant



Final deactivation point from initial lunar dust testing (> 1 month further deactivation; upper limit for activity)

Deactivated (50% RH, 25 °C) lunar simulant and lunar dust can be reactivated by exposure to UV radiation under vacuum.

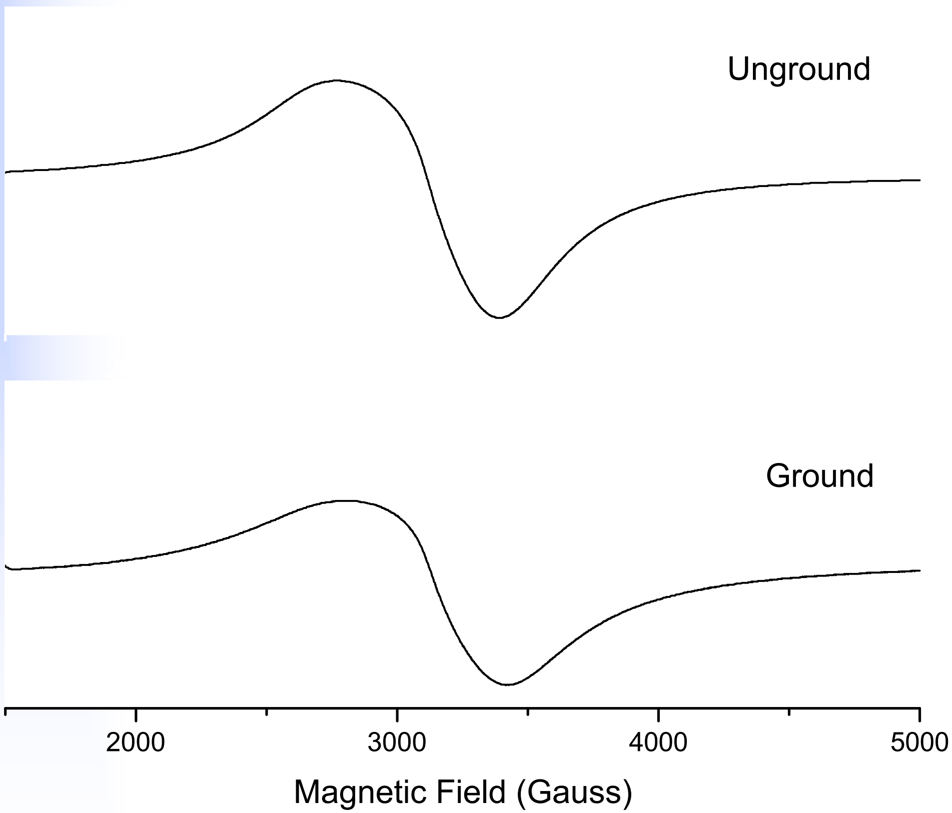
Effect of Heating Dust



- 150 ^{o}C in vacuum oven
- Six hour heating at 175 ^{o}C shows some changes; further studies underway

EPR

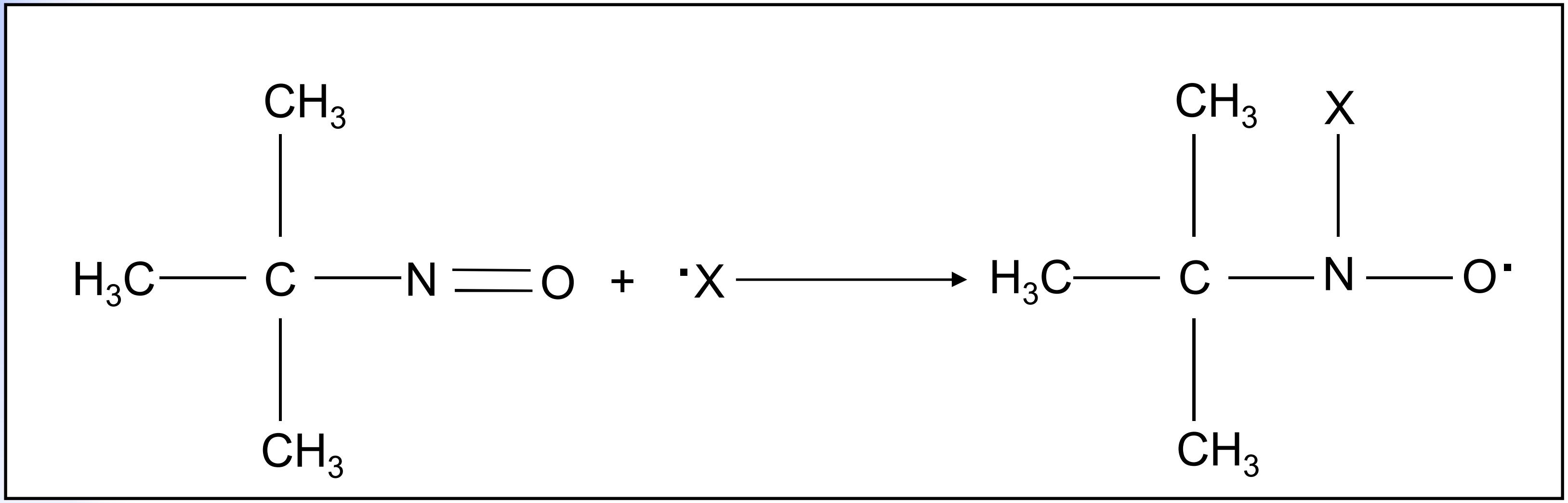
EPR Spectra of Apollo 62241



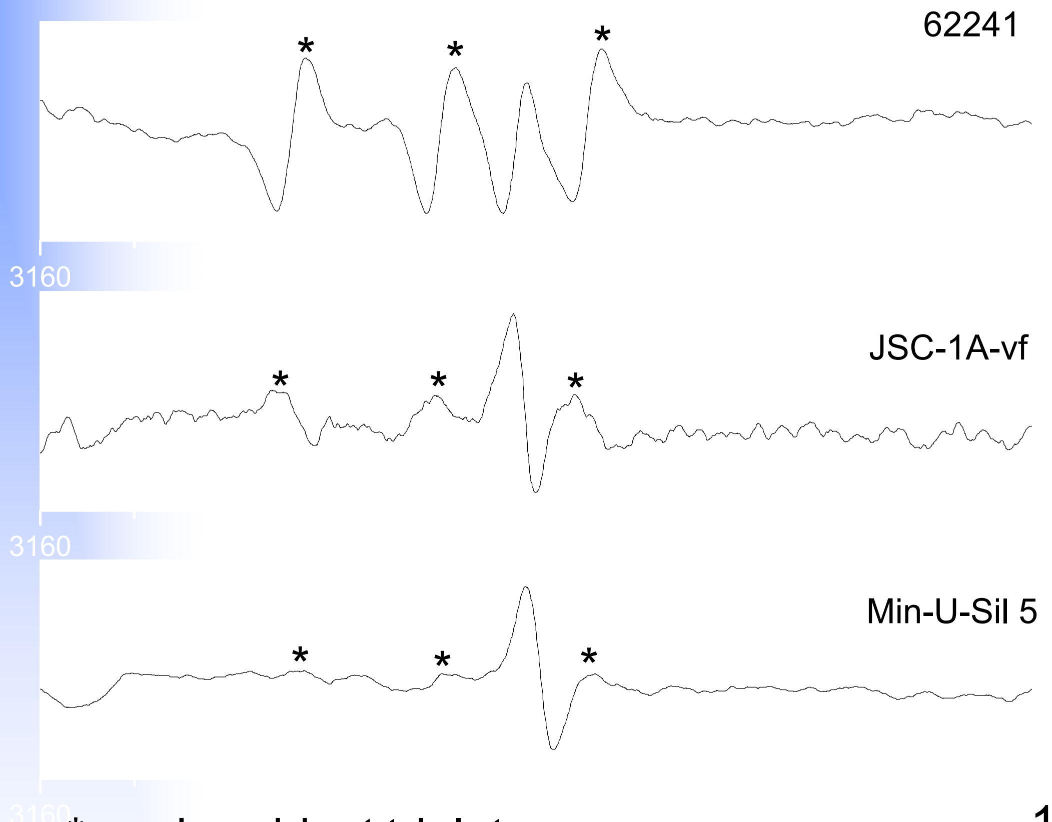
- Broad peaks: no determination of silicon- or oxygen-based radicals
- Change in g-values from 2.11 (unground) to 2.09 (ground)
- Similar downward shifts and g-values seen previously by Haneman and Miller*

*: D. Haneman and D.J. Miller, *Proc. Second Lunar Sci. Conf.* **3** (1971) 2529-2541.

MNP Spin-adduct Reaction



Spin-trapping of Radicals



10 minute grinding

10 minute grinding

30 minute grinding

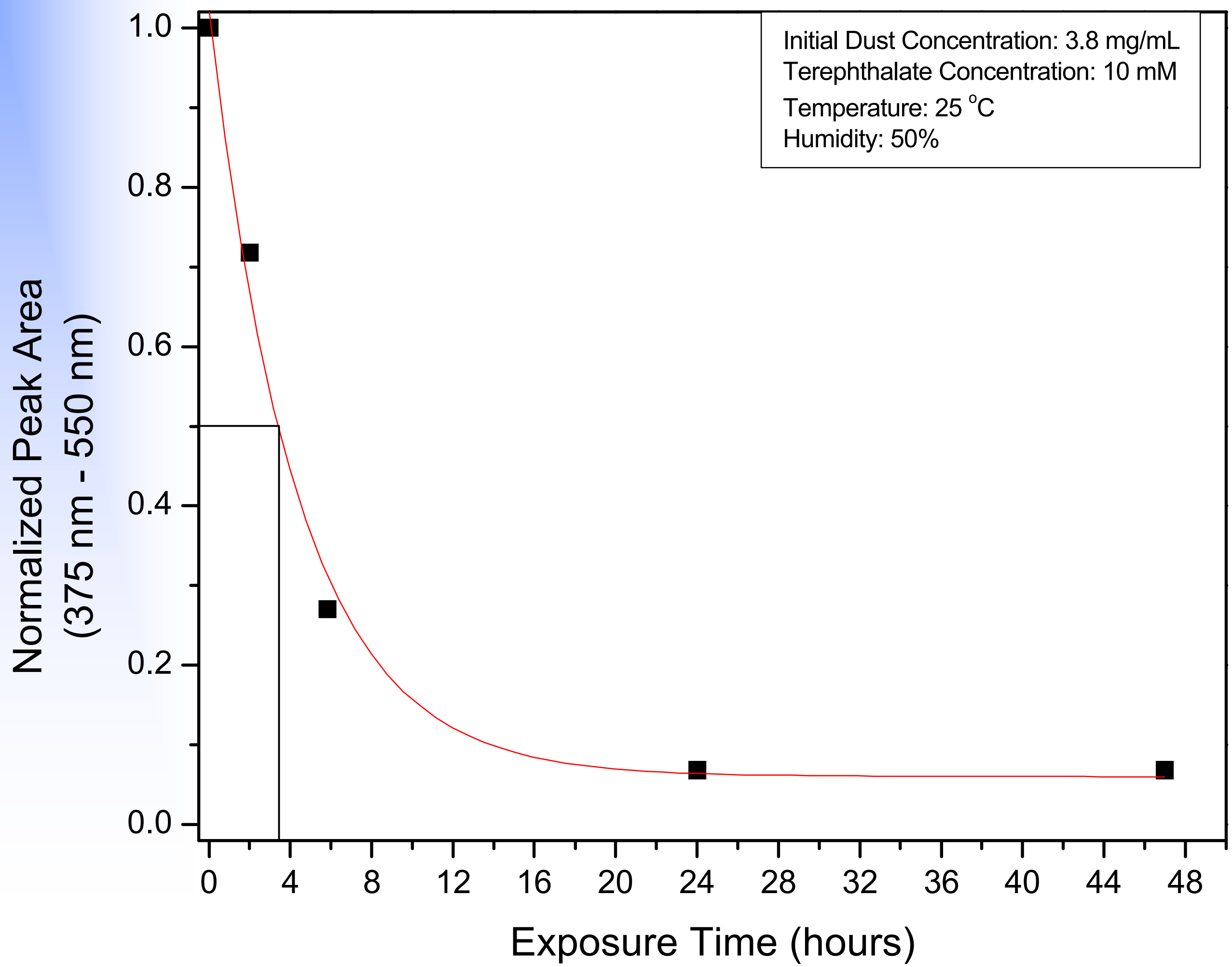
* : spin-adduct triplet

100 mM MNP/acetonitrile

- Level of activity increases in the order: quartz < lunar dust simulant < lunar dust
- Peak-to-peak splitting corresponds to radical containing no hydrogen
    - Activated species likely interacting with acetonitrile to produce radicals
- Future testing to include hydroxyl radical trap in water

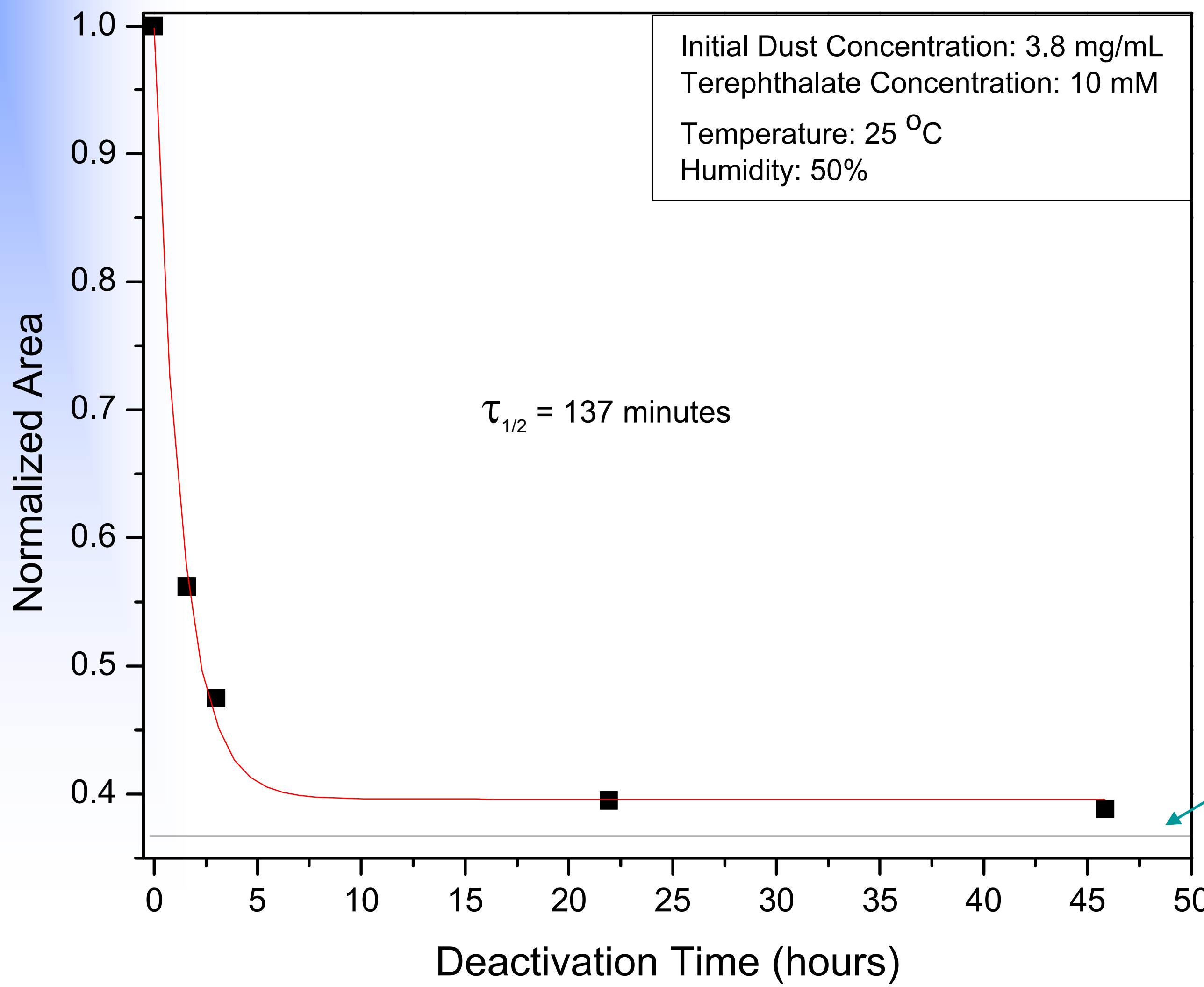
Deactivation

Deactivation of Freshly Ground Lunar Simulant (JSC-1A-vf)



- Activity of freshly ground simulant can be reduced by exposure to humid environment.
- Multiple sets of deactivation experiments show simulant half life to be ~ 3 hours with activity approaching unground levels at ~ 24 hours.

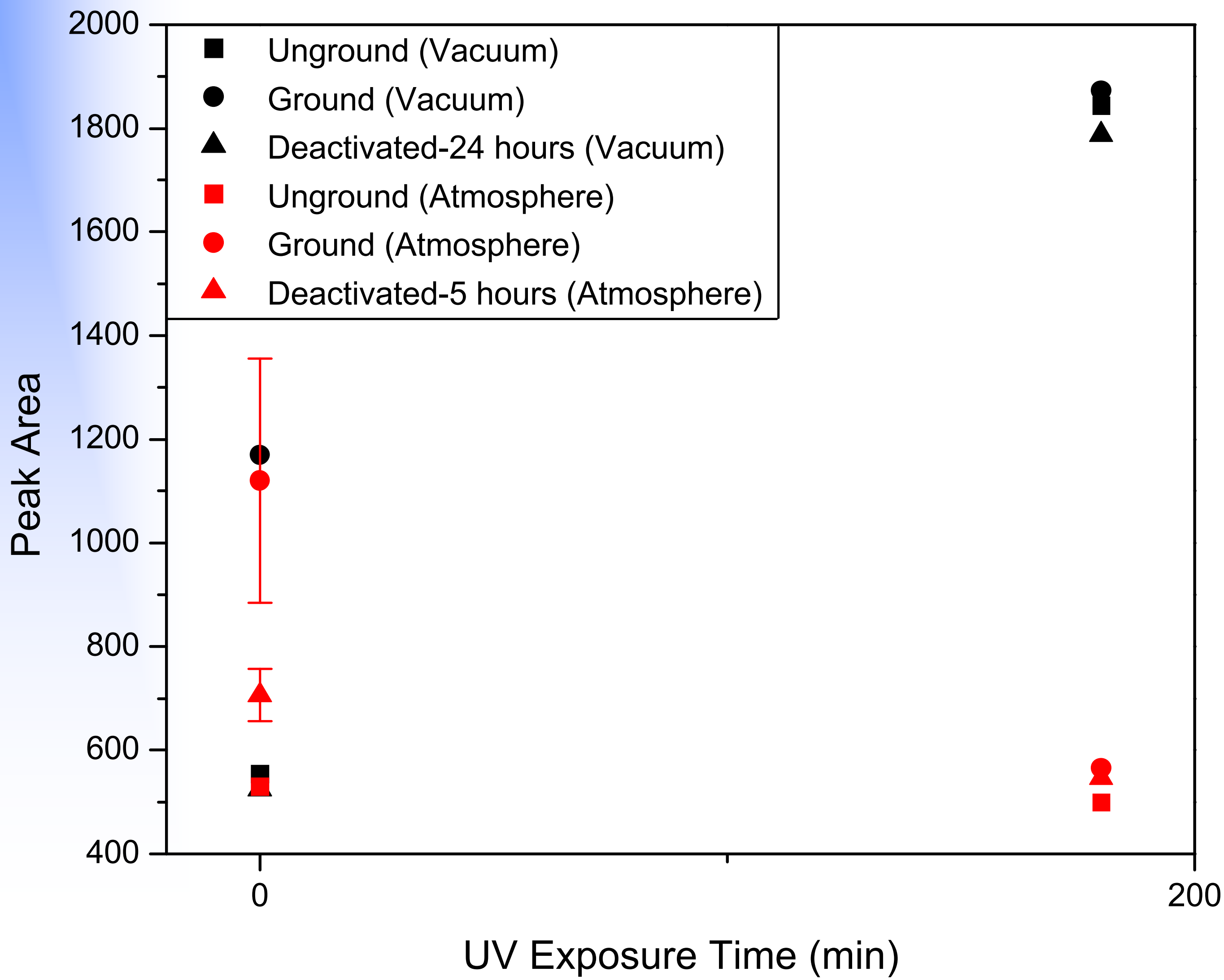
Deactivation of Freshly Ground Quartz



Much faster deactivation of quartz, especially with respect to approach of unground activity.

Activity of unground quartz (close to zero intensity; normalized to freshly ground)

Effects of Vacuum on UV Activation/Deactivation of Lunar Simulant



- 3.8 mg/mL
- 10 mM Terephthalate
- 800 W UV (initial setting)

- Error bars for deactivated and ground simulant account for activities prior to and at conclusion of UV exposure.

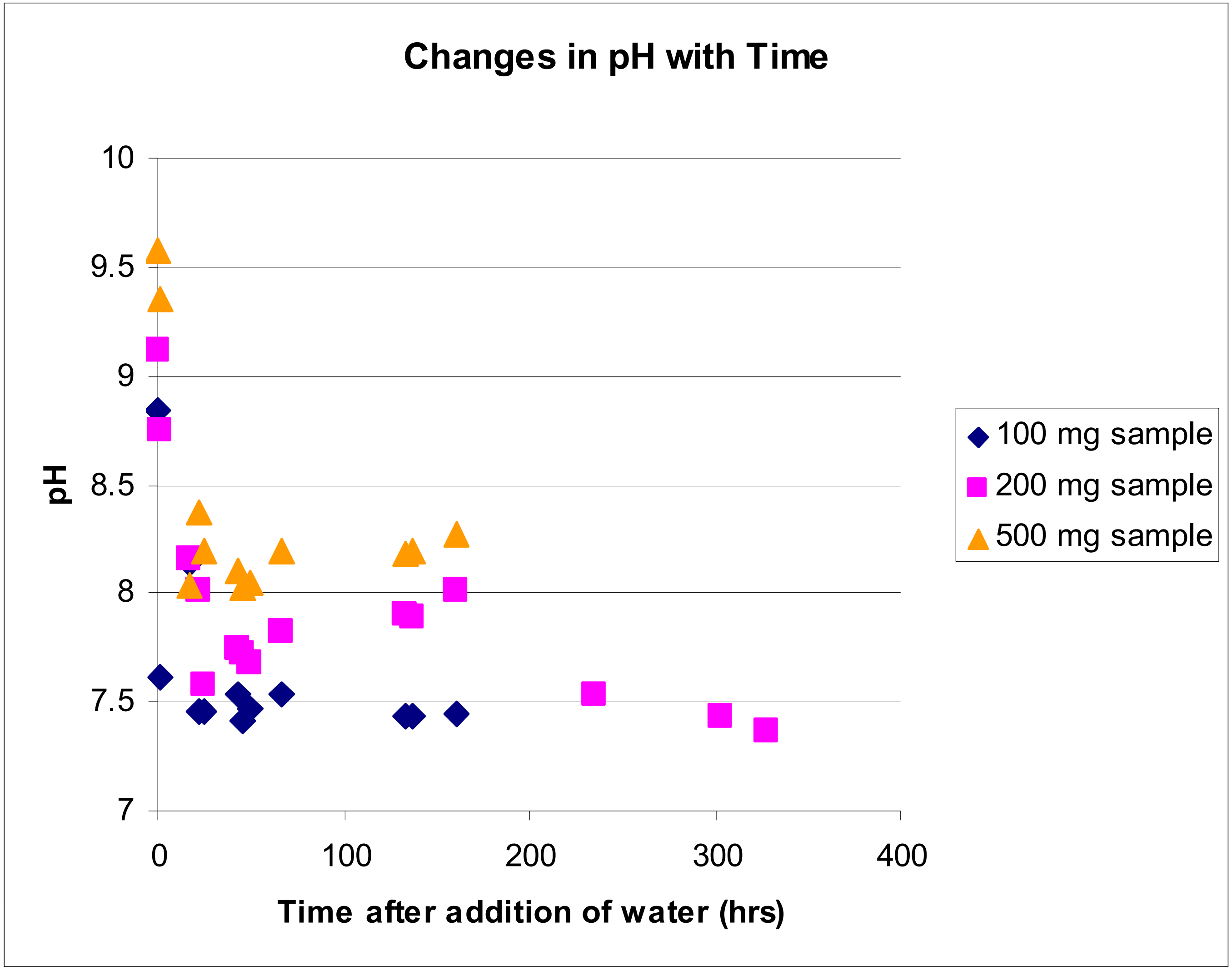
Exposure of active simulant to UV in air leads to deactivation!

Solubility

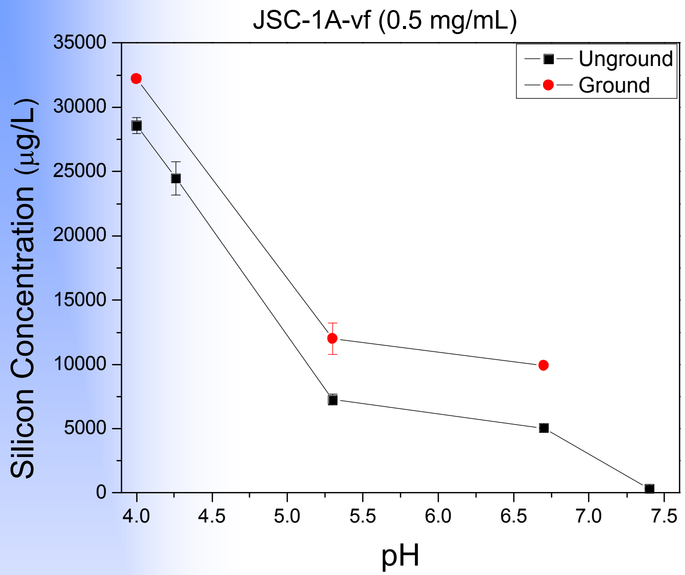
Technique

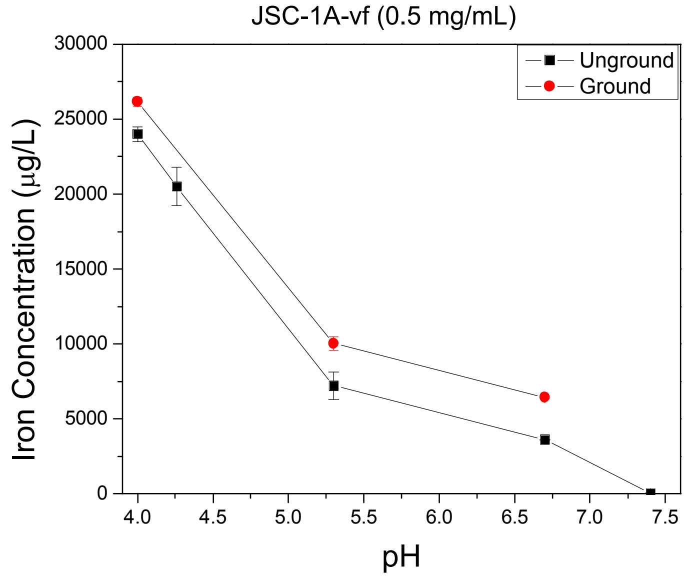
- Place 10 mg JSC-1A-vf in 20 mL of buffer solution in 50 mL centrifuge tube
- Rotate tubes for 72 hours under ambient conditions (23-25 ^{o}C, 30-50% RH)
- Flush syringes and 0.2 µm syringe filters with distilled water
- Filter solutions
- Measure concentrations using ICP-MS

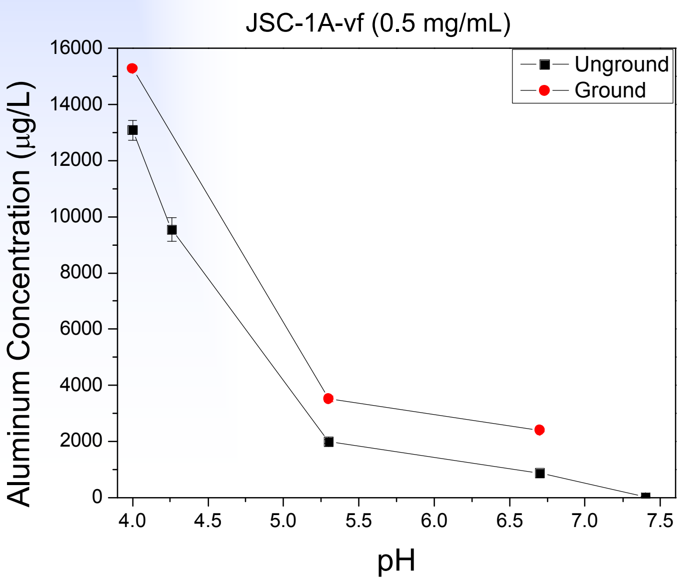
pH Effects of Simulant

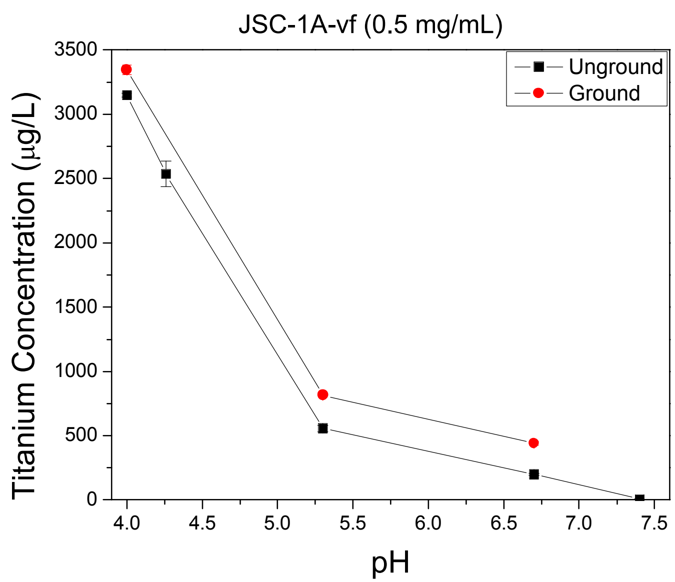


Leaching Effects of pH









- Buffer solutions were prepared at pH of 4.0, 4.26, 5.3, 6.7, and 7.4

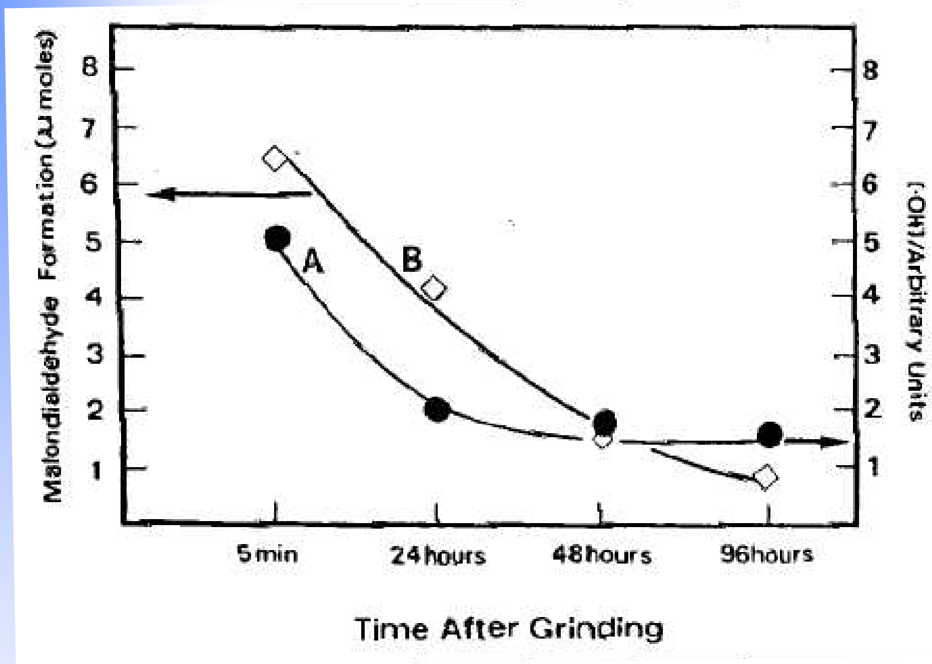
- 10 mg of unground or ground JSC-1A-vf were added to 20 mL of each buffer solution in 50 mL centrifuge tubes (0.5 mg/mL)

- Rotated slowly for 72 hours
- Filtered solutions were tested using ICP-MS
  - Si, Al, Fe, Ti, Ni, Cu, Zn, Ca, Mg, K, Na
- Ni, Cu, Zn, and Na not significantly above controls

- Future testing to include lunar dust and lung fluid simulants

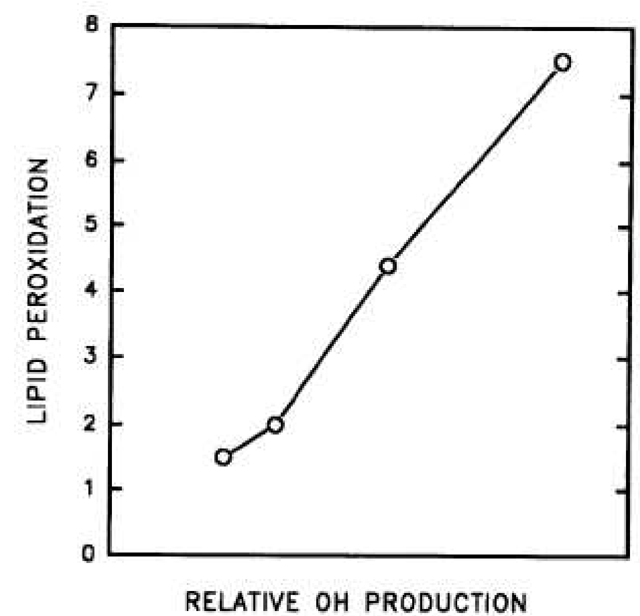
Cell Culture

Direct toxicity of Quartz



Parameter	Aged Si	Fresh Si
Hemolysis[b]	2 ± 1%	39 ± 1%
Membrane leakiness[c]	15 ± 2%	58 ± 8%
Lipid peroxidation[d]	1.5 ± 0.4 μmol mal	7.5 ± 0.6 μmol mal

- Grinding of quartz also leads to direct toxicity *in vitro*
- Ability of ground silica to oxidize lipids is directly correlated to the number of radicals produced in solution and “freshness” of silica



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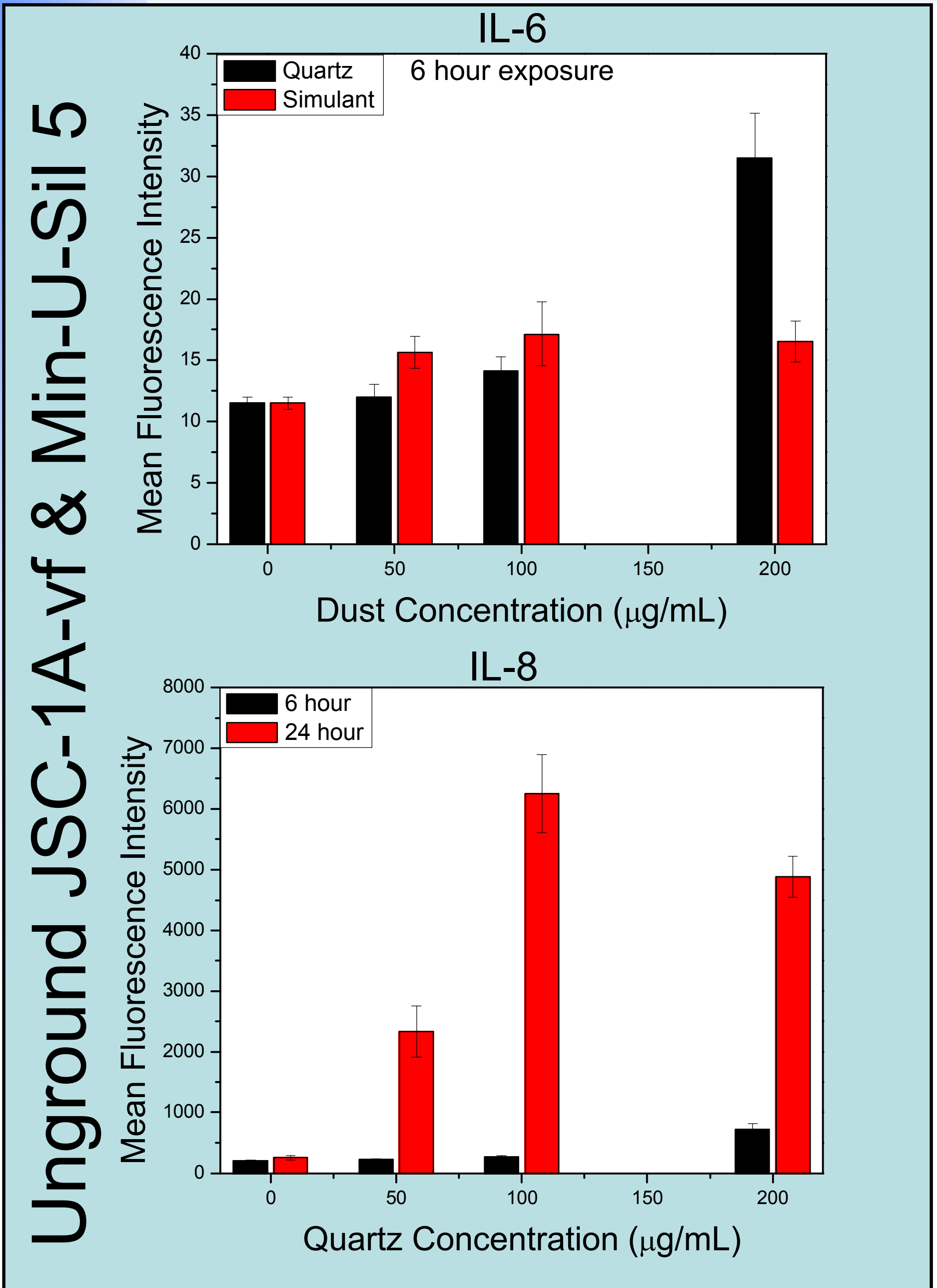
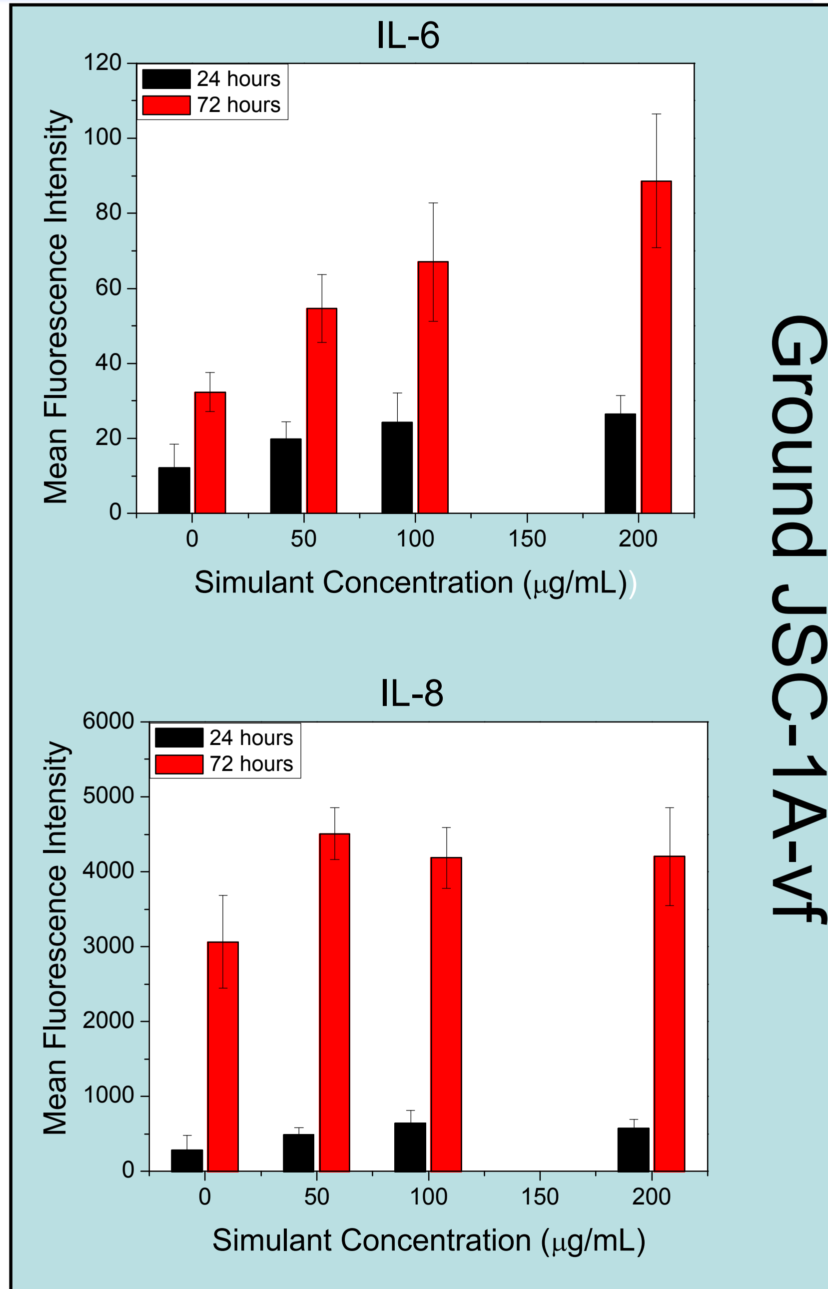
N.S. Dalal, X. Shi, and V. Vallyathan, *Free Rad. Res. Comms.* **9** (1990) 259-266.

Techniques

- A549 alveolar epithelial cells grown 72 hours
- Treatment media prepared by adding10 mg of sample to 10 mL F-12K media with no FBS
    - Dilutions prepared (200, 100, and 50 µg/mL) from stock
    - Growth media removed from cells and 1 mL treatment media added
    - Cells incubated in treatment media for 6, 24, or 72 hours
- Media removed and centrifuged (5 min, 6000 rpm) to remove dust or cellular debris
- Supernatants tested for inflammatory mediators (IL-8, IL-6, and TNF-α)
- Time dependence seen for cytokine production
- Future testing to include bronchial epithelial cells

Cytokine Production





Summary

- Grinding of lunar dust leads to the production of radicals in solution and increased dissolution of lunar simulant in buffers of different pH.
- Decreases in pH lead to increased leaching from lunar simulant
- Ground and unground lunar simulant and unground quartz have been shown to promote the production of IL-6 and IL-8, pro-inflammatory cytokines, by alveolar epithelial cells.
- These results provide evidence of the need for further studies on these materials prior to returning to the lunar surface.

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